

[o.m3.p7] Study of formation and structure of $[(Co_{0.56}Zn_{0.44})_2(PO_4)(H_{1.5}PO_4)_2]C_4H_8N_2H_4$. A. Bareges, A.N. Christensen and R.G. Hazell. *Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark*

Keywords: microporous materials.

Microporous compounds as zeolites and aluminophosphates are traditionally obtained in hydrothermal synthesis. In the synthesis of aluminophosphates from amorphous reaction mixtures organic template molecules act as structure directing compounds. Amines are often used as template molecules, and transition metal amine complexes have also been used as structure directing compounds. The framework aluminium atom can be partly substituted by divalent atoms like Mg, Zn, Co and possibly Mn. It has also been reported that framework structures of phosphates with the transition metals iron and zinc can be obtained with a number of structure directing organic amines.

The present investigation was made to study the formation of Co and Zn phosphates in solvothermal synthesis using the amine piperazine as template molecule, and the compounds $Co_7(HPO_4)_4(PO_4)_2 \cdot [Zn_2(PO_4)(H_{1.5}PO_4)_2]C_4H_8N_2H_4$ and $[(Co_{0.56}Zn_{0.44})_2(PO_4)(H_{1.5}PO_4)_2]C_4H_8N_2H_4$ were obtained. Single crystal X-ray diffraction analysis was made on one of them.

Crystallographic data for $[(Co_{0.56}Zn_{0.44})_2(PO_4)(H_{1.5}PO_4)_2]C_4H_8N_2H_4$: monoclinic cell $a = 13.4102(9)$, $b = 12.8569(9)$, $c = 8.1890(5)$ Å, $\beta = 94.634(1)^\circ$, $Z = 4$, space group $C2/c$. The Co and Zn atoms occupy one crystallographic site statistically with a tetrahedral metal-oxygen coordination and an average metal-oxygen distance of 1.941(2) Å.

[o.m3.p8] Microporous Rare-Earth Coordination Polymers: The Effect of Lanthanide Contraction on Crystal Architecture and Porosity. A. Michaelides^a, S. Skoulika^a, A. Dimos^a, C. Didierjean^b, A. Aubry^b. ^a*Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece and* ^b*Laboratoire de Cristallographie et Modelisation des Materiaux Mineraux et Biologiques (LCM3B), Universite Henri Poincare Nancy I, ESA 7036, BP 239, 54506 Vandoeuvre les Nancy Cedex, France.*

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A series of coordination polymers of lanthanides (Ln^{3+}) with adipic (H_2ad) acid were prepared.

In the case of adipic acid the compounds are of general formula $[Ln_2(ad)_3(H_2O)_x]_yH_2O$. Crystal structure analysis shows that for $Ln = Ce^{3+} - Nd^{3+}$ the compounds have the same structure as that for La^{3+} ($x=4$, $y=6$) published recently by us (*Inorg. Chem.* 1998, 37, 3407) and contains interconnected channels filled with hydrogen bonded water molecules. For $Ln = Nd^{3+} - Yb^{3+}$ the structure ($x=4$, $y=variable$) consists of interpenetrated (4,4) metal-organic networks (inclined interpenetration). However, the large angle of interpenetration creates channels whose width decreases with ionic radius (lanthanide contraction). Lattice (disordered) water was found only for $Ln = Nd^{3+}$, Sm^{3+} presenting the largest channels. The lanthanide contraction is also responsible for the passage from one structural type to the other. Five organic ligands are indeed around the metal in the structure of La^{3+} while there are only four in the second type. Furthermore, the hydrogen bond network stabilising the lanthanum adipate structure is progressively weakened when moving from La^{3+} to Nd^{3+} . It is worth noting that neodymium adipate crystallises in both structural types.

In all the above mentioned solids, water (lattice and coordinated) can be reversibly removed.